Determination of Refractive and Volatile Elements in Sediment using Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Godfred Odame Duodu[a], Ashantha Goonetilleke[b], Charlotte Allen[c] and Godwin A. Ayoko[a*]

a. School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology (QUT), 2 George St, 4001, QLD, Australia

b. School of Civil Engineering and Built Environment, Science and Engineering Faculty, Queensland University of Technology (QUT), 2 George St, 4001, QLD, Australia

c. Institute for Future Environments, Queensland University of Technology (QUT), 2 George St, 4001, QLD, Australia

Author to whom correspondence should be addressed: g.ayoko@qut.edu.au

Tel: +61 7 3138 2586

Abstract

Wet-milling protocol was employed to produce pressed powder tablets with excellent cohesion and homogeneity suitable for laser ablation (LA) analysis of volatile and refractive elements in sediment. The influence of sample preparation on analytical performance was also investigated, including sample homogeneity, accuracy and limit of detection. Milling in volatile solvent for 40 minutes ensured sample is well mixed and could reasonably recover both volatile (Hg) and refractive(Zr) elements. With the exception of Cr (-52 %) and Nb (+26 %) major, minor and trace elements in STSD-1 and MESS-3 could be analysed within ± 20 % of certified values. Applicability of the method compared with total digestion using HF was tested by analysing 10 different sediment samples. The laser method recovers significantly higher amounts of analytes such as Ag, Cd, Sn and Sn than the total digestion method making it a more robust sampling method for elements across the periodic table. LA-ICP-MS also eliminates the interferences from chemical reagents as well as the health and safety risks associated with digestion processes. Therefore, it can be considered as an enhanced method for the analysis of heterogeneous matrices such as river sediments.

Keywords: river sediment analysis; hydrogen fluoride digestion; Laser ablation; sample preparation; elemental analysis

Introduction

Heavy metals in sediments have been highlighted by several studies [1-3]. Most often, they are assessed by determining the total concentration in the sediment against some applicable national guidelines [4 & 5] or pollution indices (such as Enrichment factor (EF) and geochemical index) [3 & 6] to ascertain the level of pollution. However, total elemental determination in sediments needs to overcome the refractory nature of the minerals in some sediments (rutile and zircon, for example) [7]. Conventionally, this has been achieved by fusion at high temperatures of a fluxed, pulverized sample, or sample digestion with a mixture of acids including hydrofluoric acid (HF) or perchloric acid ($HClO_4$) followed by flame or furnace AAS [8] and ICP-OES [9] or ICP-MS [8 &10] analysis.

Concerns have been raised about the efficiency, and health and safety risks associated with these processes. The protocol is complex, time- and resource-consuming, and only moderately successful, in that incomplete dissolution is commonly observed. Further, HF and $HClO_4$ are toxic and explosive, respectively [11]. In addition, HF has been shown to attack glassware, thus contaminating the sample and weakening the glassware. Therefore, an excess amount of boric acid is subsequently required to neutralise the fluoride, which can have negative matrix effects [8; 10 & 11]. Also, isobaric interferences from chloride derived polyatomic ions in ICP-MS analysis have been observed with chloride-based acids [11 & 12]. Recoveries and precision of pseudo-total and total digestion methods vary due to many factors, including the mineral composition, the method of sample introduction as well as the identity of the elements of interest [13]. The determination of some elements (As, Sb, Se, Sn and especially volatile one like Hg) which are of environmental concern is challenging and may require the development of various specific methods for a complete multi-element analysis [14 & 15]. Consequently,

alternative methods of analysis which eliminate time-consuming digestion processes, mass interferences and associated health risk and take into consideration volatile elements, are preferred.

X-ray fluorescence (XRF) and particle induced microanalysis such as Instrumental Neutron Activation Analysis (INAA) and Scanning Electron Microscopy (SEM) are some common techniques employed for the direct analysis of elemental composition of sediments. However, XRF and SEM lack the sensitivity required for the measurement of lower atomic mass elements of interest and trace (parts per trillion to parts per billion) levels of elements in environmental samples like sediment [10]. Facilities for INAA are also not readily available due to the initial set-up cost and the stringent regulations associated with the management of such facilities coupled with issues of waste radioactive materials disposal and the relative long time required for analysis compared to XRF and ICP-MS [16].

Recently, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been established as a powerful tool for the measurement of major, minor and trace elements in environmental samples requiring minimal to no sample preparation [17-21]. Laser ablation (LA) has the added advantage of providing excellent absolute detection limits due to the consistent small size distribution of the ablated particles that are readily transported to the ICP-MS plasma torch resulting in complete decomposition [22]. Also, small amounts of samples are required for LA-ICP-MS analysis [21]. The LA-ICP-MS method provides adequate sensitivity, precision, and accuracy over a wide range of concentrations, offering an alternative for direct quantitative measurement of elements in sediment without requiring multiple digestion processes [23]. Although significant improvements have been reported in recent years, this technique is still in development.

Some arguments against LA-ICP-MS are that, the optimization of laser parameters change depending on the sample matrix [18], making the method development matrix dependent. Moreover, direct quantification is not straightforward as it is with super-dilute solution nebulisation ICP-MS due to the lack of solid calibration standards of sufficient homogeneity, particularly the ones that are matrix-matched [23]. Arroyo et al. 23] also identified the following as key limitations of the method: (a) the optimization is for a single element analysis or for a limited suite of elements; (b) sample preparation compromises the quantitation of volatile compounds; (c) sample preparation remains labour intensive and/or requires the use of binders (ie dilutants and contaminants) ; (d) complex or expensive quantitation strategies are required to improve accuracy and precision; and/ or (e) the effect of sample heterogeneity is not effectively addressed.

However, recent studies have shown that most of the issues above can be easily mitigated or proven not to be real. Laser parameters must be improved and adapted to each type of sample, from bulk metal to fine particulate powdered materials. Inexpensive solid calibration curves can be easily constructed for the measurement of major, minor and trace elements by LA-ICP-MS [24]. Simple and fast sample preparations such as fusion and pressed rock powder pellets can be utilised to determine trace and ultra-trace elements with LA [22 & 24]. Mukherjee et al. have also shown that line scans with a high repetition frequency and large beam diameter can be used with matrix-independent protocol to overcome sample heterogeneity issues [22]

Sediments have heterogeneous matrices with variable mineral and organic composition leading to analytical complexity. Grain size of <10 μm has been recognized as being important for producing homogeneous and cohesive silicate samples suitable for LA-ICP-MS without the use of binders [22 & 22]. Similarly, for granitic or samples containing resistant minerals such as zircon, extra grinding to achieve grain sizes down to <5 μm is needed for better precision for elements that are concentrated in these minerals [22]. Using a ball mill, Arroyo et al [23] dry-

ground soil and sediment samples for 40 minutes and obtained particles with an average grain size of d_{50} < 10 μm. Improvements in the particle size and grinding time were observed with a high speed mill. However, in dry milling, the container of the mill and therefore the samples become hot and may cause some loss of volatile elements. To avoid this shortcoming and to improve sample homogeneity, Garbe-Schönberg and Müller [25] applied wet-milling protocols in aqueous suspension using a planetary ball mill and agate tools to obtain nano-particulate powders with a typical grain size of d_{50} < 1.5 μm and form pressed powder tablets with excellent cohesion, homogeneity and mechanical stability suitable for laser ablation micro-analysis. Although smaller particle size was achieved with this method, samples had to be freeze dried after milling, making it time consuming and laborious. In this study, we propose the use of a volatile solvent such as ethanol to aid in the milling. This will significantly reduce sample preparation time as well as ensure good recoveries for volatile compounds.

To-date, most calibration in LA-ICP-MS is done with non-matrix matched standards such as NIST glasses. However, such calibrations may lead to systematic bias in the results for a number of elements due to issues such as internal standard concentration and distribution, ablated mass, aerosol size distribution, vaporization and ionization regions of the particles within the ICP being significantly different [25]. Also, because of the extremely inhomogeneous distribution of Pd, Pt, Ni and Se, some NIST glasses may only be suitable for bulk analytical, but not for micro-analytical purposes at very low test portion masses [26]. More importantly, no guidance exists for the measurement of Hg (which is of environmental concern) in sediment using LA-ICP-MS.

Given the need for a rapid sample preparation method for complete suite of elemental analysis in sediment by LA-ICP-MS, this paper proposes an innovative method which allows the use of sediment certified reference materials (CRMs) as calibrators for micro-analysis and incorporate recent enhancements proposed by Arroyo et al, and Garbe-Schonberg & Muller [23 & 25]. In

addition, this method is optimised and validated to cover a larger number of elements including a volatile element (Hg) which has not been reported in literature. Similarly, our method offers a simpler and faster sample preparation strategy compared to that of Garbe-Schonberg & Muller [25]. This will contribute to establishing LA-ICP-MS as a versatile technique for routine monitoring of elements in sediments at contaminated and background sites.

Materials and methods

2.1. Reagents and standards

Germanium (IV) oxide (99.99%, Aldrich) powder was used as the internal standard. Certified sediment reference materials: (a) Drainage sediment reference material, GBW07312 (IGGE, IRMA, China); (b) Marine sediment reference material, MESS-3 (National Research Council of Canada, Ottawa, Canada) and (c) Stream sediment reference material, STSD-1(National Research Council of Canada, Ottawa, Canada) were used for the optimization and evaluation of the analytical performance of the LA method. Similarly, MESS-3 and STSD-1 were used to evaluate the performance of the digestion method. Internal Standard Mix Be, Rh In and Bi (Agilent Technologies Australia Pty Ltd) was used to determine instrument drift. Ethanol undenatured 100% AR (Chem-Supply Pty Ltd, Australia) was used as solvent for milling while HNO_3, HF and HCl (all from RCI Labscan, Bacto Laboratories Pty Ltd Australia), and ultrapure water (UPW) with 18.2 MΩ-cm resistivity (Merck Millipore, Australia) were used for digestion.

2.2. Sample preparation for LA-ICP-MS analysis

About 10g of coarse sediment samples were pulverised down to fine grains (< 150 μm) for 30 seconds in a Bench Top Ring Mill BTRM (ROCKLABS, New Zealand) with a double discus high chrome steel head.

Homogenization and milling of samples to grain size < 10 μm was achieved with a vibratory McCrone Micronizing mill (Illinois , USA, powered by a 1/30 HP motor) with inert 125 mL capacity polypropylene jar grinding vessel fitted with a screw-capped, gasketless, polypropylene cap with PTFE liner. The jar was packed with an ordered array of identical, cylindrical six regular layers of eight agate grinding elements. Samples for homogenization included certified sediment standards as received from certifying institutions or collected river sediment samples after pulverization with BTRM. Precisely 40 mg of germanium (IV) oxide was added to a known mass of sediment such that the mass of Ge ~ 1%. The mixture was loaded into the micronizing mill and 8 mL of undenatured ethanol added, homogenised for 40 minutes with 30 seconds pause every 5 minutes for cooling. The vial was then opened and slurry sample transferred to a plastic petri dish. Vial and balls were carefully rinsed with undenatured ethanol until the rinsing liquid collected from the vial was clear. The slurry sample was placed in a sealed oven at 40 ^{O}C to speed up drying. Complete drying was achieved between 4 to 8 hours depending on the amount of solvent added.

Approximately 1 g of the dry homogenized sample powder was loaded into a manual tablet press (SPECAC Manual Hydraulic Press 25.000, Kent, UK) with a 13 mm die set and formed into a pellet of about 12 mm diameter and 2 mm thick by applying a force not more than 8 ton for 1 min.

2.3. Sample preparation for solution-ICP-MS analysis

About 3 drops of double distilled 2% HNO_3 was added to a Teflon beaker to reduce the electrostatic effect and 100 mg of samples weighed into it using weighing paper. Additionally, 3 mL of double distilled HNO_3 was added to the sample in the beaker, capped and left on a hot plate at 120 ^{o}C overnight. The cap was removed and the sample was dried on the hot plate at 100 ^{o}C. Afterwards, 1.5 mL of double distilled HCl, 0.5 mL of double distilled HNO_3, and 0.5 mL of double distilled HF were added, capped and left on the hot plate at100 ^{o}C for about 15

minutes. The beaker was taken off the hot plate and pressure build up was released by loosening the cap. The capped beaker and its content were left on the hot plate at 125 ^{o}C overnight, again. The beaker was then opened and solution left to evaporate on the hot plate to incipient dryness at 80 ^{o}C. Subsequently, 2 mL of double distilled HCl was added, capped and left on the hot plate at 100 ^{o}C for 15 minutes. The beaker was taken off the hot plate and pressure build up was released by loosening the cap. The beaker was capped, returned to the hot plate and left overnight at 100 ^{o}C. It was again dried at 100 ^{o}C, l mL double distilled HNO_3 added, dried at 100 ^{o}C, 1 mL of ultrapure water (UPW) and 1mL of double distilled HNO_3 added and dried at 100 ^{o}C. Finally, 0.20 mL of double distilled HNO_3 and 4.80 mL of UPW were added to the beaker, capped and left on the hot plate to reflux at 125 ^{o}C overnight. The sample was transferred to a centrifuge tube and centrifuged at 1900 g for 15 minutes. Aliquots of the sample was taken and analysed after the addition of the internal standard.

2.4. Grain size analysis by laser diffraction

For particle size determination, samples were added to the dispersing unit containing water such that obscuration was between ~5-10%, while the suspension was being sonicated. Measurements were carried out using Malvern Mastersizer 3000 applying the Mie scattering model with three reading cycles and cycle duration of 1 minute.

2.5 LA-ICP-MS analysis

A 193 nm ArF excimer laser ablation system (Electro Scientific Industries, New Wave Research Division, Tokyo, Japan) coupled to an Agilent 8800 Triple Quad ICP-MS (Agilent Technologies Australia Pty Ltd) were used for the measurements. Samples were loaded into a 3-D printed cell specifically designed to avoid movement of samples during ablation. Different laser parameters including repetition rates (6 Hz, 8 Hz, 10 Hz), ablation modes (single spot, depth profile, line, raster), fluence (3 to 4 mJ cm^{-2}) and spot sizes (80, 100, 150 μm) were evaluated. The best ablation results, evaluated as the best precision and accuracy for reference

standards, were obtained using 8 Hz, line ablation mode with 100 μm spot size and laser fluence between 3.2 and 3.4 mJ cm^{-2}. Samples were carried from the cell into the Ar carrier gas with 0.85 L min^{-1} He. Furthermore a diatomic gas (N_2) was added to increase the sensitivity, particularly of the light masses at the rate of 14 mL min^{-1} using a mass flow meter (ALICAT SCIENTIFIC, Scitek Australia Pty Ltd). No formal signal smoothing device was employed to resolve the pulsing laser other than an extra 2 metres of tygon tubing to transport the aerosol to the plasma. Operating conditions of both laser and ICP-MS are summarized in Table 1. LA data were processed with Igor Pro version 6.34 coupled to Iolite 2.5 software [27] using external calibration with natural sediments GBW07312 and STSD-1, and Ge as internal standard. The ICP-MS was calibrated to low oxide production rates ($ThO^+/Th^+ < 0.5$ %, using NIST 610, and 612), which was monitored throughout batch acquisition. All data were background corrected and four replicate measurements were taken for each sample.

Table 1. LA-ICP-MS and solution ICP-MS instrument operating conditions.

LA-ICP-MS Parameters		Digestion ICP-MS Parameters	
Plasma conditions		*Plasma conditions*	
RF Power	1350 W	RF Power	1550 W
no gas, single quad mode		Sampling depth	8.0 mm
Sample depth	5.0 mm	Carrier gas (Ar) flow	1.05 L min^{-1}
Carrier gas (He) flow	0.85 L min^{-1}		
Optional gas (N_2)	14.0 mL min^{-1}		
Laser conditions		*Collision/Reaction Cell conditions*	
Fluence	3 - 4 mJ cm^{-2}	He gas flow	5 mL min^{-1}
Pulse frequency	8 Hz	Octopole bias	18.0 V for He mode and -8.0 V for no gas mode
Spot size	100 μm	Kinetic Energy Discrimination	5.0 V
Wash time	40 s		

2.6 Solution-ICP-MS analysis

Samples were analysed using an Agilent 8800 Triple Quadrupole ICP-MS (Agilent Technologies Australia Pty Ltd). Calibration solution was prepared from digested USGS

geological reference material W-2a (dolerite) with Be, Rh, In and Bi as internal standards for instrument drift correction. Natural sediments MESS-3 and STSD-1 were analysed as unknowns to assess the accuracy of measurement. Elements that suffer from polyatomic interferences (e.g. ^{65}Cu: $^{32}S^{16}O_2{}^1H^+$, $^{40}Ar^{25}Mg^+$, $^{40}Ca^{16}O^1H^+$, $^{36}Ar^{14}N_2{}^1H^+$) were acquired in He mode. However, elements that do not suffer from polyatomic interferences in common matrices were acquired with no added reaction gas. Operating conditions of ICP-MS are summarized in Table 1 above.

Results and Discussion

3.1. LA-ICP-MS Sample preparation

Accurate results depend largely on both standards for calibration and unknown samples having similar matrices. A protocol must demonstrate accuracy at a relatively high level (from 80 to 120 % for sediment analysis) to be acceptable. Many analyses with LA-ICP-MS are done with NIST glass standards because these materials are well characterized for most elements of the periodic table, and the glasses are homogenous. However, except for silicate minerals and other glasses, they are not matrix-matched with other materials. This introduces systematic, but unknown bias into the analysis. Sediment is a complex matrix with variable grain size and mineral composition. To-date, there is no commercially available “micro” sediment standard suitable for direct laser ablation analysis without the use of a binder. Grain size of certified sediment standards can be up to 200 μm which requires further grinding to smaller grain sizes with a more limited grain size distribution to be used as calibration standard. This was achieved with a McCrone Micronizing mill.

The grinding mechanism in a McCrone Micronizing mill move agate element with respect to its neighbours between the plane ends and along the cylindrical sides. During grinding, the slurry continuously circulates between these surfaces providing a more rapid grinding than a

ball mill. Also, the slurry helps to ensure that none of the sample compacts into corners where it escapes the grinding elements. Agate ball elements are considerably pure but they can be sources of contamination of Ag, Cs, W and U [28]. However, the slurry helps to reduce abrasions on the grinding elements which can introduce contamination.

Total grinding times of 10, 20, 30 and 40 minutes were investigated at intervals of 5 minutes milling and 30 seconds cooling to avoid overheating of the sample. Solvent to sample ratio of ~ 3 was maintained throughout the experiment. This was in the range of 2.5 – 6 which was reported to be effective for milling by Garbe-Schonberg & Muller [25]. Table 2 shows the grain size distribution as read from a cumulative size distribution plot when GBW07312 was used as a test sample. The 50% (d_{50}) and 90% (d_{90}) grain size distribution for 10 and 40 minutes grinding improved from 3.65 µm and 10.80 µm to 2.38 µm and 5.80 µm, respectively. The smaller and narrow range of grain size distribution after 40 minutes milling enhanced the cohesiveness of the pressed tablet samples giving a much more stable transient signal during ablation. In addition, the smaller and narrow range of grain size distribution led to ablated samples that could be readily transported to the ICP-MS plasma torch and resulted in the complete decomposition to enhance the detection limits [22]. Also, the recovery of most elements improved significantly. The overall precision of analysis (homogeneity) also improved from 28.34, 19.65, 14.54 and 6.82% RSD for grinding times of 10, 20, 30 and 40 minutes, respectively, for STSD-1 when GBW07312 was used as the calibrator. Similar observations were made by Mukherjee et al and Arroyo et al. [22 & 23]. For heterogeneous samples such as sediment which could contain hard and soft mineral mixtures, 40 minutes grinding in the agate mill was effective in producing efficient grain size and ensured better mixing that is highly recommended for granitic samples and use of smaller laser spot sizes. This agrees with the recommendation made by Mukherjee et al. [22]

Table 2. Grain size distribution of GBW07312 after wet milling

Grinding time (minutes)	d_{10} [μm]	d_{50}[μm]	d_{90}[μm]
0 (Original sample)	3.47	7.76	38.1
10	0.96	3.65	10.8
20	0.89	2.9	7.98
30	0.88	2.75	7.52
40	0.83	2.38	5.8

3.2. Method calibration for LA-ICP-MS

Various calibration strategies have been adopted for LA-ICP-MS, some of which are simple and rapid. However, most of these strategies do not facilitate the use of LA-ICP-MS as a stand-alone technique or require adopting inter-elemental correction for measurement of elements of environmental concern. Germanium has been employed as the internal standard in the form of GeO_2 powder instead of the common crustal elements such as Ca, Si and Fe, which could vary from sample to sample. The reasons for the choice of internal standard element are clarified by Arroyo et al. [23]. In this study, the same relative mass of GeO_2 was added to matrix-matched standard as well as each sample such that Ge is ~ 1%. This technique assumes that in the natural sample, Ge content is by far less than one weight percent of the element. Subsequent milling and homogenization processes ensured Ge is evenly distributed in the samples making it ideal for calibration. The accuracy and precision of the method was measured by percentage recovery and percentage relative standard deviation, respectively, when GBW07312 (for STSD-1), and GBW07312 and STSD-1 (for MESS-3), were used as calibrators (see Table 3 and 4)

3.3. Analytical recovery of elements in sediment CRMs by LA-ICP-MS

Analyses of pressed pellets of certified sediment standards STSD-1 and MESS-3 as determined by the calibrators GBW07312 and/or STSD-1 were used to ascertain the accuracy, precision and sensitivity of our method. These sediments are quite different in their mineral content. Accuracy was measured as percentage recovery (measured/certified) while precision was expressed as relative standard deviation and limit of detection (LOD) was used as a measure of sensitivity. Since the amount of material ablated in LA sampling is normally different for each acquisition, LODs are different for each sample and must be calculated for individual acquisition [29]. The LOD was calculated using Iolite software at the 99% confidence level, determined as three times the standard deviation of the background measurements [26 & 29]. The value reported (Table 3 and 4) is a mean value for 7 replicates of the LOD obtained after running the STSD-1, MESS-3 as well as sand (quartz) blank [23]. A total of 47 elements across the periodic table covering major, minor and trace analytes, most of which are of environmental concern were measured using LA-ICP-MS.

As evident from Table 3, all major elements analysed were within ± 19 % of the certified values and typically ± 5 % for K, Mn, Na, Ti and Fe in STSD-1, and Mn in MESS-3. Similarly, RSD and LOD were < 11 % and < 20 $\mu g g^{-1}$, respectively, for all major elements with LOD typically < 10 $\mu g g^{-1}$ except for Fe and Si which were 11.70 and 19.39 $\mu g g^{-1}$, respectively. The accuracy was generally lower for Si, but far better for Fe when compared with the study by Arroyo et al. [23]. However, no LOD was reported for these elements by Arroyo et al., but the LOD calculated for these elements and the major elements in general was very low (in the order of 0.03-1) when compared to XRF data provided by McComb et al. [30]

Data from Table 4 equally shows that minor and trace elements in STSD-1 and MESS-3 could be analysed within ± 20 % of certified values excluding Cr (-52 %) and Nb (+26 %). Similar trend was observed by Leite et al. [24] with Cr deviating from the certified value by -25%.

Precision was typically <10% RSD for the minor and trace elements. The only exceptions were Au, Ni, Th and Y (in STSD-1), which were >10%, but <18%. However, detection limit for the minor and trace elements typically ranged between 1-10 parts per billion (ngg^{-1}) with Au even going down to 10 parts per trillion. The only exceptions were five elements Cr (10.88 ngg^{-1}), Lu (10.25 ngg^{-1}), Nd (15.66 ngg^{-1}), V (10.29 ngg^{-1}) and Yb (24.08 ngg^{-1}). Nevertheless, the LOD recorded were very low compared to previous studies [23; 24 & 26] and similar to that stated by Mukherjee et al [22].

It could be observed that the method gave good recovery and precision with low LOD for elements such as As, Hg, Sn, Sb and Se which usually require the addition of hydride system to atomic spectrometers (AAS, ICP-OES or ICP-MS) to enhance their detection [31 & 32]. Also, the result indicates that sample preparation step is clean as most ultra-trace elements such as Hg, Se, Ag, Cd, Sb, Au and Tl gave good recovery and could be analysed within ±20% of certified values with precision <18% RSD.

Table 3. Recovery, relative standard deviation and detection limit of major elements in STSD-1 and MESS-3 by LA-ICP-MS.

	STSD-1				MESS-3				LOD
Element	Certified value ($\mu g\ g^{-1}$)	This work ($\mu g\ g^{-1}$)	% RSD	% Recovery	Certified value ($\mu g\ g^{-1}$)	This Work ($\mu g\ g^{-1}$)	% RSD	% Recovery	($\mu g\ g^{-1}$)
Al	45882	37400	9.8	81.51	85764.71	99150	2.1	115.61	0.08
Ca	25714	23865	1.9	92.81					0.01
Fe	47000	48633.33	3.4	103.48	43060	57400	1.6	133.3	1.17
K	9957	10060	7.7	101.03					0.44
Mg	13200	11030	6.5	83.56					0.01
Mn	3950	4050	1.7	102.53	365	348	10.5	95.34	0.05
Na	13355	13270	7.6	99.36					0.49
Si	198333	231000	6.8	116.47	277200	252050	5.8	90.93	19.39
Ti	4600	4373.25	3.5	95.07					0.06

LOD – Limit of detection.

Table 4. Recovery, relative standard deviation and detection limit of minor and trace elements in STSD-1 and MESS-3 by LA-ICP-MS.

	STSD-1				MESS-3				LOD
Element	Certified value ($\mu g\ g^{-1}$)	This work ($\mu g\ g^{-1}$)	% RSD	% Recovery	Certified value ($\mu g\ g^{-1}$)	This Work ($\mu g\ g^{-1}$)	% RSD	% Recovery	($ng\ g^{-1}$)
Ag	<0.5	0.46	4.152	92.00	0.18	0.19	0.010	105.56	3.77
As	23	23.99	5.381	104.30	20.70	20.82	0.403	100.58	0.94
Au	0.008	0.0096	17.424	119.58					0.01
Cd	0.8*	0.90	9.754	112.50	0.24	0.24	0.024	100.00	0.20
Ce	51	48.86	1.411	95.80					2.37
Co	17	16.70	3.830	98.24	13.80	13.92	0.243	100.87	1.87
Cr	67	40.60	3.623	60.60	106.00	50.50	1.564	47.64	10.88
Cs	1.8	1.78	2.810	98.89					9.57
Cu	36	36.68	3.224	101.88	39.30	40.13	0.661	102.11	3.08
Dy	5.6	5.49	3.474	98.04					9.08
Eu	1.6	1.61	0.751	100.63					4.47
Hf	6.1	5.20	4.390	85.25					4.15
Hg					0.09	0.08	0.013	88.89	2.40
La	30	29.84	4.623	99.48					2.54
Li	11	11.21	1.133	101.91	73.90	71.37	2.054	96.58	2.34
Lu	0.8	0.81	0.642	100.77					10.25
Nb	5	6.29	5.234	125.70					0.18
Nd	28	27.74	3.090	99.07					15.66
Ni	24	23.64	14.544	98.50	49.30	49.70	5.908	100.81	1.45
Pb	35	37.86	3.963	108.17	21.90	22.83	0.962	104.25	3.03
Rb	30	28.70	3.551	95.67					4.74
Sb	3.3	2.66	3.402	80.61	1.09	1.10	0.064	100.92	9.81
Sc	14	15.31	4.423	109.32					9.57
Se					0.72	0.69	0.051	95.83	6.25
Sm	6	6.38	2.360	106.33					8.66
Sn	4	4.23	7.490	105.75	2.27	2.46	0.312	108.37	1.03
Sr	170	168.90	6.722	99.35	125.00	127.03	5.635	101.62	2.46
Ta	0.4	0.40	1.390	100.25					1.64
Tb	1.2	0.99	7.181	82.50					6.72
Th	3.7	4.09	12.080	110.54					3.78
Tl					0.98	1.14	0.013	116.33	1.04
U	8	9.33	6.033	116.63					6.51
V	98	97.03	8.282	99.01	252.00	250.68	8.184	99.48	10.29
W	4	4.55	2.601	113.73					0.22
Y	42	43.53	13.552	103.64					1.12
Yb	4	4.12	1.543	103.00					24.08
Zn	178	182.10	3.441	102.30	172.00	171.68	8.640	99.81	7.36
Zr	218	219.73	4.740	100.79					3.08

LOD – Limit of detection, * – Partial extraction

3.4. Analytical results of digestion method

Table 5 gives information about the accuracy and precision of the total digestion method. Accuracy and precision were measured as percentage recovery and percentage relative standard deviation, respectively. Only minor and trace elements in STSD-1 and MESS-3 were analysed to evaluate the accuracy and efficiency of the digestion method. Au and Hg were not detected, while the result for As and Se were not reliable and consequently, excluded from the data.

Out of the 35 elements analysed, 26 could be determined within ±20% of the certified values. However, recovery for Ag (26.36%), Cd (61.59%), Hf (67.28%), Lu (68.27%), Nb (125.37%), Sn (3%), Tl (129.59%), W (16.16%) and Zr (77.11%) were either above or below acceptable accuracy (80-120%) for digestion of sediments and soils [13]. On the other hand, precision was very high for the digestion method, typically <5% RSD. The LOD of the digestion method was calculated at the 99% confidence level, determined as 3 times the standard deviation of the method blank. The values reported (Table 5) is the mean values for 10 replicates of the LOD obtained after running the method blank. It ranged from 0.01(for Hf, Ta and Y) to 0.13 $\mu g g^{-1}$ for Ti. This was low compared to the data reported by Arroyo et al. [23].

Table 5 Recovery and relative standard deviation for elements (μg g^{-1}) in STSD-1 and MESS-3 using HF digestion

	STSD-1				MESS-3				
Element	Certified value (μg g^{-1})	This Work (μg g^{-1})	% RSD	% Recovery	Certified value (μg g^{-1})	This Work (μg g^{-1})	% RSD	% Recovery	LOD (μg g^{-1})
Ag	0.50	0.13	1.111	26.36	0.18	0.08	1.428	46.68	0.03
Ba	630.00	614.17	2.358	97.49					1.82
Cd	0.8*	0.49	0.709	61.25	0.24	0.15	3.078	62.48	0.08
Ce	51.00	49.85	0.178	97.75					0.07
Co	17.00	16.89	0.335	99.34	13.80	13.38	2.477	96.96	0.61
Cr	67.00	59.45	0.437	88.74	106.00	99.21	0.750	93.59	8.29
Cs	1.80	1.75	1.405	97.31					0.06
Cu	36.00	35.44	1.185	98.43	39.30	40.58	0.551	103.25	0.81
Dy	5.60	5.51	1.552	98.34					0.04
Eu	1.60	1.58	1.084	98.44					0.03
Hf	6.10	4.10	0.742	67.28					0.01
La	30.00	29.77	3.985	99.25					0.08
Li	11.00	12.14	0.474	110.36	73.90	68.70	0.695	92.96	2.51
Lu	0.80	0.55	1.631	68.27					0.03
Nb	5.00	6.27	0.812	125.37					0.04
Nd	28.00	32.35	1.188	115.52					0.04
Ni	24.00	25.64	0.453	106.83	49.30	44.18	0.713	89.61	2.21
Pb	35.00	38.70	2.244	110.57	21.90	21.80	0.414	99.56	0.79
Rb	30.00	32.06	0.642	106.85					0.26
Sb	3.30	2.83	0.198	85.77	1.09	1.06	1.491	97.42	0.24
Sc	14.00	13.01	3.574	92.93					0.28
Sm	6.00	6.84	0.898	113.97					0.04
Sn	4.00	0.12	4.024	3.09	2.27	0.16	2.209	6.99	0.77
Sr	170.00	186.46	0.427	109.68	125.00	133.47	1.138	106.77	0.57
Ta	0.40	0.37	1.881	91.82					0.01
Tb	1.20	0.95	2.193	79.56					0.03
Th	3.70	3.65	1.012	98.69					0.06
Ti	4600.00	3930.45	1.009	85.44					13.38
Tl					0.98	1.27	0.951	129.59	0.09
U	8.00	7.43	0.612	92.93					0.03
V	98.00	89.96	0.711	91.80	252.00	218.90	1.262	86.86	0.62
W	4.00	0.65	1.737	16.16					0.02
Y	42.00	38.52	2.971	91.71					0.11
Yb	4.00	3.26	1.765	81.56					0.03
Zn	178.00	171.56	0.472	96.38	172.00	142.81	0.981	83.03	9.74
Zr	218.00	168.09	1.230	77.11					0.24

*Partial extraction

3.5 Comparison of Laser ablation and total digestion methods.

Figure 1: Ratio plot of LA-ICP-MS (dash line) and HF digestion (solid line) measurements to certified values of the STSD-1 analysed.

Compared to HF digestion (solid line), majority of the elements plotted were close to unity with a few deviations within ±20% of the certified value for the LA-ICP-MS (Figure 1). Only Cr and Nb deviated from within ±20% which is normally accepted for measurement of soils and sediments [16]. On the other hand, the ratio for many elements was far from unity for the digestion method. The deviation from unity was appreciable (> ±30%) for Ag, Cd, Hf, Lu, Sn and W. Barring the isolated high deviation of Cr and Nb, there was good agreement between the LA-ICP-MS measurements and certified reference values. Similarly, the LOD for the LA method was far superior (in the order of 10-100 fold) to the digestion method. Arroyo et al. also observed likewise where LOD of the LA was similar or better than the digestion method [23]. It should be mentioned that the LOD reported for the LA method is by far the best in comparison to the past results reported by Mukherjee et al [22]. This could be due to the narrow range of particle size after milling. However, as expected, precision of the digestion method were generally better than the LA-ICP-MS (Table 4 and 5).

3.6 Analysis of river sediment by LA and solution ICP-MS

Sediment samples obtained from ten different sampling sites from the Brisbane River (Australia) were analysed to assess how the two methods compare with each other. According to the textural charts proposed by Folk (1954), the sediments sampled (Table 6) could be grouped into four categories; sand (SPM-22), muddy sand (SPM-10), sandy mud (SPM-8) and sandy silt (SPM-3, SPM-7, SPM-9, SPM-17, SPM-18, SPM-19 and SPM-20) [33]. The average content of organic carbon in the sediment ranged between 0.06 to 0.77 wt% (Table 6).

Table 6 Site location and sedimentary features of the Brisbane River sediment

	Location		Sedimentary features (%)			
Sample	Latitude	Longitude	Organic carbon	Clay	Silt	Sand
SPM-3	27°35'52.77"S	152°51'37.26"E	0.13	11.49	42.88	45.66
SPM-7	27°33'12.89"S	152°54'6.45"E	0.65	18.23	60.36	21.42
SPM-8	27°32'32.05"S	152°55'21.97"E	0.32	21.65	56.84	21.53
SPM-9	27°31'27.69"S	152°55'33.26"E	0.39	19.93	63.57	16.45
SPM-10	27°31'39.47"S	152°56'43.34"E	0.06	16.86	30.08	53.06
SPM-17	27°28'45.69"S	153° 2'58.27"E	0.77	16.81	64.67	18.53
SPM-18	27°28'21.16"S	153° 3'12.68"E	0.35	18.9	66.06	15.08
SPM-19	27°26'13.07"S	153° 6'56.40"E	0.53	12.74	48.67	38.61
SPM-20	27°26'26.49"S	153° 7'27.70"E	0.46	13.29	60.57	26.11
SPM-22	27°21'42.13"S	153° 9'21.08"E	0.13	1.06	3.81	95.16

A total of 28 elements from across the periodic table, excluding the major elements were analysed. The detailed results are shown in Table S1 to S4 in the Supplementary information. The laser ablation method was measured against the established HF digestion method and reported as ratio (LA/HF). The two methods compare well at each sampling site as the ratio of most elements was close to unity except Ag, Cd, Nb, Sn, Tl and Cu (at SPM-17 and SPM-18). The precision, measured as %RSD for all elements were within the acceptable range for sediment analyses at all the sampling sites which were typically <10% for both methods except Cd which was > 20% at or below detection limit (0.08 μgg-1). This implies that the sediment sub-sampling and preparation produced a homogenous sample at the scale of laser sampling (tens of microns) and is comparable with the bulk digestion for the solution technique.

In the LA method, the sample transported to the ICP is dry. On the other hand, in the solution method, samples are highly solvated. Addition of water to the plasma can lead to the formation of oxide (MO^+) and hydride (MH^+) which causes polyatomic interferences [34]. This could reduce the count rate for the ultra-trace elements so that counts are variable, near their detection limit. For these elements (Ag and Cd), the LA method appears superior and recorded higher concentrations than the HF digestion. From Tables 4 and 5, it could be observed that the

LA and HF methods recovered higher values of Nb and Tl respectively than the certified values. It is therefore not surprising that the ratio (LA/HF) of Nb and Tl are above and below unity, respectively. However, the results of Cu at SPM-17 and SPM-18 should be treated with caution as no explanation could be given for the high deviation of Cu from unity at these sites. The laser method recorded higher concentration of Sn at all sampling sites compared to the digestion method. This is expected as the HF digestion under-recovered Sn in the certified materials STSD-1 and MESS-3 (Table 5).

In addition to the comparison of accuracy and precision, statistical analyses (ANOVA and Spearman rank correlation coefficient (rho), were used to determine if there were significant differences and correlation of the elements at the sampling sites for both methods. Table S5 and S6 in the Supplementary information shows a summary of the ANOVA and Spearman rank correlation coefficient values, respectively. ANOVA analysis confirmed that with the exception of Cu (at SPM-17 and SPM-18) and Nb (at SPM-18), the differences in the mean values ($n = 3$ and 4 for digestion and LA, respectively) at each site are not beyond the explanation of sampling variability alone at 95 % confidence level ($P < 0.05$).

Among the 28 elements analysed, 27 showed positive correlation between the digestion and LA method with their rho values ranging from 0.67 up to 1.00. Nevertheless, Sn was different, showing a negative correlation, because its Spearman rho value was negative (-0.21) and below the critical value of 0.649 [35].

Conclusions

The wet-milling employed produced powdered sediment with typical grain size d_{50} <3 μm allowing the formation of pressed powder tablets with excellent cohesion and homogeneity suitable for laser ablation sampling without the use of a binder. Although this sample preparation is relatively long (about five hours) compared to the established fusion method

(about an hour or less), this method is worth the trade-off for the improvement reported. Hg and Zr in sediment could be measured (accurately and precisely) with LA-ICP-MS using a single sample preparation, the first of its kind to be reported in published literature to the best of our knowledge. This opens new avenue for the measurement of volatile elements such as F, Cl, Br and S, where very limited published data exist and are partly inconsistent with one another and for Ru, Os, and I for which no data exist at present. Also LOD down to parts per trillion could be obtained with this method. In addition, it will save resources as LA-ICP-MS could be used for multi-element analysis without requiring the development of different methods for different elements.

Analytical results obtained by LA-ICP-MS were comparable to total digestion followed by ICP-MS analysis. The sample preparation offers the opportunity to measure major, minor and trace elements in sediments with reasonable accuracy and precision with the exception of Cr and Nb. Additionally, LA can be considered an exhaustive sampling method that recovers significantly higher amounts of analytes such as Ag, Cd, Hg, Sn, Sb and Se compared to the total digestion method. This eliminates interferences from chemical reagents as well as the safety and health risks associated with digestion processes.

Supplementary Information

The Supplementary information provides data derived on the comparison of the HF method and LA method and statistical treatment to differentiate the HF and LA methods.

Acknowledgement

We thank Queensland University of Technology and Ghana Atomic Energy Commission for providing scholarship and study leave, respectively, for the first author to undertake this study. We also express our gratitude to the Central Analytical Research Facility (CARF) for

providing the facilities and to Irina Kinaev and Karine Harumi Moromizato for providing training on solution and laser sampling using ICP-MS, respectively.

References

[1] Ahmed, F., Bibi, M. H., Seto, K., Ishiga, H., Fukushima, T. and Roser, B. P. (2010). Abundances, Distribution, and Sources of Trace Metals in Nakaumi-Honjo Coastal Lagoon Sediments, Japan. Environ. Monit. Assess., 167(1-4): 473-491.

[2] Waltham, N. J., Teasdale, P. R., and Connolly, R. M. (2011). Contaminants in water, sediment and fish biomonitor species from natural and artificial estuarine habitats along the urbanized Gold Coast, Queensland. J. Environ. Monit., 13(12): 3409-3419.

[3] Cevik, F., Goksu, M.Z.L., Derici, O.B., Fındık, O. (2009). An assessment of metal pollution in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses. Environ. Monit. Assess., 152: 309–317.

[4] Beegany, C. and Bay, S. M. (2012). Transitioning Sediment Quality Assessment into Regulations: Challenges and Solutions in Implementing California's Sediment Quality Objectives. Integrated Environmental Assessment and Management, 8(4): 586–588

[5] Burton, G. A., Jr. (2002). Sediment Quality Criteria in Use Around the World. Limnology, 3(2): 65-75.

[6] Duodu, G. O., Anim, A. K., Serfor-Armah, Y. and Sarfo, D.K. (2011). Assessment of the levels of toxic and potentially toxic metals in sediments from the weija dam Ghana. Elixir Pollution, 38: 4320-4324.

[7] Baker, S.A., Bi, M., Aucelio, R.Q., Smith, B.W., Winefordner, J.D., (1999).Analysis of soil and sediment samples by laser ablation inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom., 14: 19-26.

[8] Daskalakis, K. D. and O'Connor, T. P. (1995). Normalization and Elemental Sediment Contamination in the Coastal United States. Environ. Sci. Techno., 29: 470-477.

[9] Vicente-Martorell, J. J., Galindo-Riano, M. D., García-Vargas, M., Granado-Castro, M. D. (2009). Bioavailability of heavy metals monitoring water, sediments and fish species from a polluted estuary. Journal of Hazardous Materials, 162: 823–836

[10] Accornero, A., Gnerre, R., and Manfra, L. (2008). Sediment Concentrations of Trace Metals in the Berre Lagoon (France): An Assessment of Contamination. Arch Environ Contam Toxicol, 54: 372–385.

[11] Hassan, N. M., Rasmussen, P. E., Dabek-Zlotorzynska, E., Celo, V. and Chen, H. (2007). Analysis of Environmental Samples Using Microwave-Assisted Acid Digestion and Inductively Coupled Plasma Mass Spectrometry: Maximizing Total Element Recoveries. Water Air Soil Pollut., 178: 323–334.

[12] Wang, J., Nakazato, T., Sakanishi, K., Yamada, O., Tao, H., & Saito, I. (2004). Microwave digestion with HNO3/H2O2 mixture at high temperatures for determination of trace elements in coal by ICP-OES and ICP-MS. Analytica Chimica Acta, 514: 115–124.

[13] Chen, M. and Ma, L.Q. (2001). Comparison of three aqua regia digestion methods for twenty Florida soils. Soil Science Society of America Journal, 65: 491–499.

[14] Kubrakova, I. (1997). Microwave-assisted sample preparation and preconcentration for ETAAS, Spectrochim. Acta part B, 52: 1469 -1481

[15] Chen, M. and Ma, L.Q. (1998). Comparison of four EPA digestion methods for metal analysis using certified and Florida soils. J. Environ. Qual., 27: 1294–1300.

[16] Filby, R. H., (1995). Isotopic and nuclear analytical techniques in biological systems: A critical study-IX. Neutron activation analysis (Technical Report). Pure & Appl. Chem., 67(11): 1929-1941.

[17] Günther, D.; Hattendorf, B. (2005). Solid sample analysis using laser ablation inductively coupled plasma mass spectrometry. Trends Anal. Chem., 24: 255-265.

[18] Müller, B. and Guillong, M. (2010). Laser Ablation ICP-MS Analysis of Marine Sediments from the Oxfordian (Late Jurassic): A Comparison of Three Preparation Techniques. The Open Mineralogy Journal, 4: 9-19

[19] Santos, M. C., Wagner, M., Wu, B, Scheider, J, Oehlmann, J., Cadore, S, Becker, J. S. (2009). Biomonitoring of metal contamination in a marine prosobranch snail (Nassarius reticulatus) by imaging laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Talanta, 80: 428–433.

[20] Yi-Ling, L., Chao-Chiang, C., Shiuh-Jen, J. (2003). Laser ablation inductively coupled plasma mass spectrometry for the determination of trace elements in soil. Spectrochimica Acta Part B, 58: 523–530.

[21] Pettke, T., Oberli, F., Audétat, A., Guillong, M., Simon, A. C., Hanley, J. J., and Klemm, L. M. (2012). Recent developments in element concentration and isotope ratio analysis of individual fluid inclusions by laser ablation single and multiple collector ICP-MS. Ore Geology Reviews, 44:10–38.

[22] Mukherjee, P. K., Khanna, P. P., & Saini, N. K. (2014). Rapid Determination of Trace and Ultra Trace Level Elements in Diverse Silicate Rocks in Pressed Powder Pellet Targets by LA-ICP-MS using a Matrix-Independent Protocol. Geostandards and Geoanalytical Research, 38(3): 363-379.

[23] Arroyo, L., Trejos, T., Gardinali, P. R., and Almirall, J. R. (2009). Optimization and validation of a Laser Ablation Inductively Coupled Plasma Mass Spectrometry method for the routine analysis of soils and sediments. Spectrochimica Acta Part B: Atomic Spectroscopy, 64: 16-25.

[24] Leite, T. D. F., Escalfoni Jr, R., da Fonseca, T. C. O., & Miekeley, N. (2011). Determination of major, minor and trace elements in rock samples by laser ablation inductively coupled plasma mass spectrometry: Progress in the utilization of borate glasses as targets. Spectrochimica Acta Part B: Atomic Spectroscopy, 66(5): 314-320.

[25] Garbe-Schonberg, D., & Muller, S. (2014). Nano-particulate pressed powder tablets for LA-ICP-MS. Journal of Analytical Atomic Spectrometry, 29(6): 990-1000.

[26] Jacob, D. E. (2006). High Sensitivity Analysis of Trace Element-Poor Geological Reference Glasses by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). Geostandards and Geoanalytical Research, 30(3): 221-235.

[27] Paton, C., Hellstrom, J., Paul, B., Woodhead, J. and Hergt, J. (2011). Iolite: Freeware for the visualisation and processing of mass spectrometric data. J. Anal. At. Spectrom., 26: 2508-2518.

[28] Takamasa, A. and Nakai, S., (2009). Contamination introduced during rock sample powdering: Effects from different mill materials on trace element contamination Geochemical Journal, 43: 389 – 394

[29] Longerich, H. P., Jackson, S. E., & Gunther, D. (1996). Inter-laboratory note. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. Journal of Analytical Atomic Spectrometry, 11(9): 899-904.

[30] McComb, J. Q., Rogers, C., Han, F. X., & Tchounwou, P. B. (2014). Rapid screening of heavy metals and trace elements in environmental samples using portable X-ray fluorescence spectrometer, A comparative study. Water, air, and soil pollution, 225(12): 2169-2176.

[31] Geoff T., Agnès C., Sébastien V., András B., Maria B. Concomitant Metals Analyser for Improving Productivity of an ICP-OES. Horiba Technical Reports. English Edition No.7, 38-43.

[32] Dos Santos, E. J., Herrmann, A. B., Azzolin Frescura, V. L., & Curtius, A. J. (2005). Simultaneous determination of As, Hg, Sb, Se and Sn in sediments by slurry sampling axial view inductively coupled plasma optical emission spectrometry using on-line chemical vapor generation with internal standardization. Journal of Analytical Atomic Spectrometry, 20(6): 538-543.

[33] Folk, R. L. (1954). The Distinction between Grain Size and Mineral Composition in Sedimentary-Rock Nomenclature. The Journal of Geology, 62(4): 344-359

[34] Niu, H., & Houk, R. S. (1996). Fundamental aspects of ion extraction in inductively coupled plasma mass spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy, 51*(8), 779-815.

[35] Miller, J. N., and Miller, J. C. (2010). Statistics and Chemometrics for Analytical Chemistry (Sixth ed) Pearson, Harlow